PB87-209235

IACP (Integrated Air Cancer Project) Emissions: Transformations and Fate

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jul 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-209235

EPA/600/D-87/211
July 1987

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/D-87/211	2.	3. RECIPIENT'S ACCESSION NO. PB87 209235/AS
4. TITLE AND SUBTITLE IACP EMISSIONS: TRANSFORMATIONS AND FATE		5. REPORT DATE July 1987
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) L. Cupitt, L. D. Claxton, P. B. Shepson * and T. E. Kleindienst *		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS ASRL & HERL U.S. EPA, RTP, NC 27711 Northrop Services Inc.* RTP, NC 27709		10. PROGRAM ELEMENT NO. A101/C/83/02 5097 (FY-87)
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP,NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

As part of the Integrated Air Cancer Project (IACP), diluted emissions from wood stoves and automobiles were injected into a Teflon smog chamber and irradiated to simulate their photochemical transformation in the atmosphere. Changes in the chemical composition and physical properties of the gaseous and aerosol-bound complex mixtures were monitored throughout the experiments. The mutagenicity of the gas-phase components and of the aerosol-bound chemicals were both measured before and after irradiation. Transformation of the dilute wood smoke occurred readily under all conditions tested: with and without added NO, with artifical illumination and with natural sunlight, at outdoor temperatures or at room temperature. As the photochemical reactions progressed, the volume of the aerosol-bound organics was seen to increase, suggesting that transformation products were condensing to form additional aerosol-phase materials. The photochemical transformations caused a dramatic change in the mutagenic activity of the gas-phase components. Comparisons of the mutagenic activity between the gas-phase and aerosol-bound chemicals have been estimated. When the mutagenicity is expressed in units of revertants per cubic meter of air, the gas-phase reaction products are found to be the most mutagenic. Similar results were obtained from preliminary experiments using an idling automobile as the pollutant source.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 11
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

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Diluted emissions from wood stoves and automobiles were irradiated in a Teflon smog chamber to simulate their photochemical transformation in the atmosphere. Throughout the experiments, the chemical composition and physical properties of the gaseous and aerosol-bound complex mixtures were monitored. The mutagenicity of the gas-phase components and of the aerosol-bound chemicals were measured both before and after irradiation. Transformation of the dilute wood smoke occurred readily under all conditions tested: with and without added NO, with artificial illumination and with natural sunlight, at outdoor temperatures or at room temperature. As the photochemical reactions progressed, the volume of the aerosol-bound organics was seen to increase, suggesting that transformation products were condensing to form additional aerosol-phase materials.

The gas-phase reactants and products were tested for mutagenic activity by exposing Salmonella typhimurium, strains TA 98 and TA 100, to the filtered effluent. Filter samples of the starting materials and the transformed products were collected, extracted, and tested for mutagenic activity in the same bacterial strains by using a standard plate incorporation test. The transformations caused a dramatic change in the mutagenic activity of the gas-phase components. Comparisons of the mutagenic activity between the gas-phase and aerosol-bound chemicals have been estimated. When the mutagenicity is expressed in units of revertants per cubic meter of air, the gas-phase reaction products are found to be the most mutagenic.

Introduction

The Integrated Air Cancer Project (IACP) has focused on emissions from residential wood combustion (RWC) and from automobiles. As a part of the IACP, simulation experiments were conducted to characterize the atmospheric transformations of these complex mixtures. This research effort focused on three main questions: (1) Are transformations likely to occur? (2) If transformations do occur, what changes in chemistry and mutagenicity are induced? and (3) What is the relationship between gaseous and aerosol-bound mutagens?

Experimental Methods

A schematic diagram of the 22.7 m^3 reaction chamber used for most of these experiments is shown in Figure 1. The chamber is housed in a truck trailer and consists of a 7.5 m long cylinder of Teflon film suspended between two aluminum end plates, each of which is coated with fluorocarbon paint. Irradiation is accomplished by means of blacklight and sunlamp fluorescent bulbs which surround the chamber. Oak logs, from the Research Triangle Park area of North Carolina, were burned in a commercially available wood stove. A portion of the wood smoke was introduced into a dilution tunnel and mixed with ambient air to cool the mixture. The diluted emissions were then used to fill the chamber to the desired concentration.[1] A few, preliminary experiments have recently been conducted using automobile emissions. The experimental set up is identical to Figure 1, except that the wood stove was replaced by a 1980 catalyst-equipped Toyota Corolla operating at high idle conditions and burning a "super unleaded" grade of gasoline. For a few wood smoke irradiations, a 9.0 m^3 outdoor Teflon smog chamber was used. The outdoor chamber was at ambient temperatures and used only natural sunlight.

Four chambers were used for exposure of Salmonella typhimurium, strains TA 98 and TA 100, to the various gaseous mixtures. The chambers are 190-L, rectangular, Teflon-coated containers capable of holding more than 50 test plates. "Survivor" plates were routinely included for detection of toxicity effects. The test mixtures were flushed through the bioassay exposure chambers at 14 L min^{-1}, and exposures of the bacteria to the gaseous mutagens was accomplished simply by uncovering the glass Petri dishes containing the bacteria and permitting the mutagenic materials to dissolve into the plates. If one assumes that the "dose" is proportional to the exposure period, a type of dose-response curve can be generated conveniently by allowing various groups of plates to remain uncovered for differing periods of time. The details of the mutagenicity testing have been described elsewhere.[1-3] Particulate samples from each of the test streams were collected on Teflon-coated glass fiber filters identical to those used in the ambient IACP field study. Mutagenicity testing of the particulate extracts was accomplished using the Ames standard plate incorporation test.[4] Four distinctive air streams were tested: the clean air used to replenish the chamber as samples were withdrawn, the ambient air used in the dilution tunnel, the reactants (i.e., the diluted wood smoke or auto exhaust prior to irradiation), and the chamber effluent (i.e., the diluted emissions after irradiation).

In several experiments, two bioassay exposure chambers were used in series to test the effluent from the reaction chamber. Not all of the gaseous mutagens entering the first bioassay exposure chamber are removed by the test plates. Data from the second chamber permits a better estimate of the total vapor-phase mutagenicity in the test air stream. The calculated gaseous mutagenicity may still be a lower limit estimate, however, since non-polar mutagens are not likely to be efficiently removed, even by two chambers in series.

The experiments were conducted by filling the reaction chamber with the wood smoke or automotive emissions to the desired concentration (~15 ppm Carbon), adjusting the NO_x concentration, if necessary, and then irradiating the mixture until an ozone maximum was reached. The lights were then turned off, and the effluent bioassay exposures were begun. For most of the wood smoke irradiations, additional NO was added to the system to increase the extent of reaction and to bring the hydrocarbon to NO_x ratio more in line with those measured in urban and suburban areas.[5] Additional NO was not needed for the experiments involving automotive exhaust. Irradiation of the outdoor chamber was controlled by removal and re-installation of an opaque cover. The wood smoke irradiations usually took from one to two hours to reach the ozone maximum, while the automotive exhaust experiment was irradiated for about 5 hours. The bioassay exposures typically lasted up to 10 hours. Throughout the bioassay exposure period, the sample withdrawn from the reaction chamber had to be continuously replaced with clean air. This meant that the mutagens in the reaction chamber became more and more dilute with time (~4.5% per hour). An "effective" exposure time was calculated for the effluent bioassay chamber to account for the effects of dilution.

Results

Changes in the chemical composition and mutagenic potency were readily observed for all irradiation conditions. Table I lists the initial and final concentrations of a variety of chemicals observed during three of the wood smoke irradiations. Experiment A was conducted with dilute wood smoke alone, while experiments B and C contained additional NO_x. The addition of NO_x to the dilute wood smoke irradiations caused the system to react more completely and to produce even more mutagenic products than did Experiment A. Similar experiments conducted in the outdoor chamber gave essentially identical results for both chemistry and mutagenicity, despite differences in the light intensity and distribution and the somewhat lower (by 9x C) temperatures. Irradiation of the wood smoke mixture caused the aerosol volume distribution to increase, suggesting that transformation products may be condensing out on the aerosols. The mutagenicity of both the gas-phase and the aerosol components were measured before and after irradiation. When two bioassay exposure chambers were used in series to measure the gas-phase mutagenicity, the response in the second chamber was about 30% of that in the first chamber. This implies that the bioassay exposure chamber is around 70% efficient at removing the mutagens.

Figure 2 shows the comparison of the mutagenicity associated with the gas-phase and the aerosol-bound organics, both before and after irradiation. The mutagenicity in Figure 2 is reported in revertants m^{-3} and is shown for direct acting mutagens (i.e., without metabolic activation) in two bacterial

strains (TA 98 and TA 100). Prior to irradiation, the bulk of the mutagenicity was found in the particulate phase. After irradiation, however, the gaseous transformation products contribute significantly (80 to 99%) to the total mutagenic burden in the air. It should also be noted that the mutagenic products proved to be very stable in the reaction chambers. As described in the previous section, dose response curves were derived from exposures which lasted as long as 10 hours after the lights were turned off. The dose response curves remained linear over this time period, implying that the mutagenic vapor-phase products are long lived.

Insertion of an XAD-2 trap into the line between the irradiation chamber and the bioassay exposure chamber caused the mutagenic response to decrease by more than 80%. Unfortunately, only about 10% of the removed mutagenicity was recovered in the XAD-2 extract. Many of the vapor-phase mutagens removed by XAD-2 may either be unstable on the adsorbent, or may be lost during the extraction and concentration procedures.

A series of preliminary experiments were also conducted using diluted exhaust from an idling automobile to fill the simulation chamber. Once again, the gas-phase transformation products dominated the total mutagenic burden after irradiation.

Conclusions

Irradiations of complex mixtures involving both wood smoke and automobile exhaust have demonstrated that chemical reactions are probable and that the gas-phase products which result from these chemical reactions can constitute the major portion of the total atmospheric mutagenic burden. Chemical and mutagenic changes were observed for all tested conditions (with and without added NO_x; artificial or natural illumination; controlled indoor environment or cooler outdoor temperatures), but the mutagenic response seems to increase with increasing chemical reaction. The mutagenic gas-phase products have been shown to be quite stable in the simulation chambers, with lifetimes considerably longer than many residential exchange rates.[6] These results suggest that transformation of the gas-phase and aerosol components of complex mixtures may contribute significantly to the total burden of mutagens or carcinogens in the environment and should be considered in assessing risk.

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Table I. IACP Transformation Study: Gas Phase Concentrations of Chemicals During Wood Smoke Irradiations (ppb, v/v)

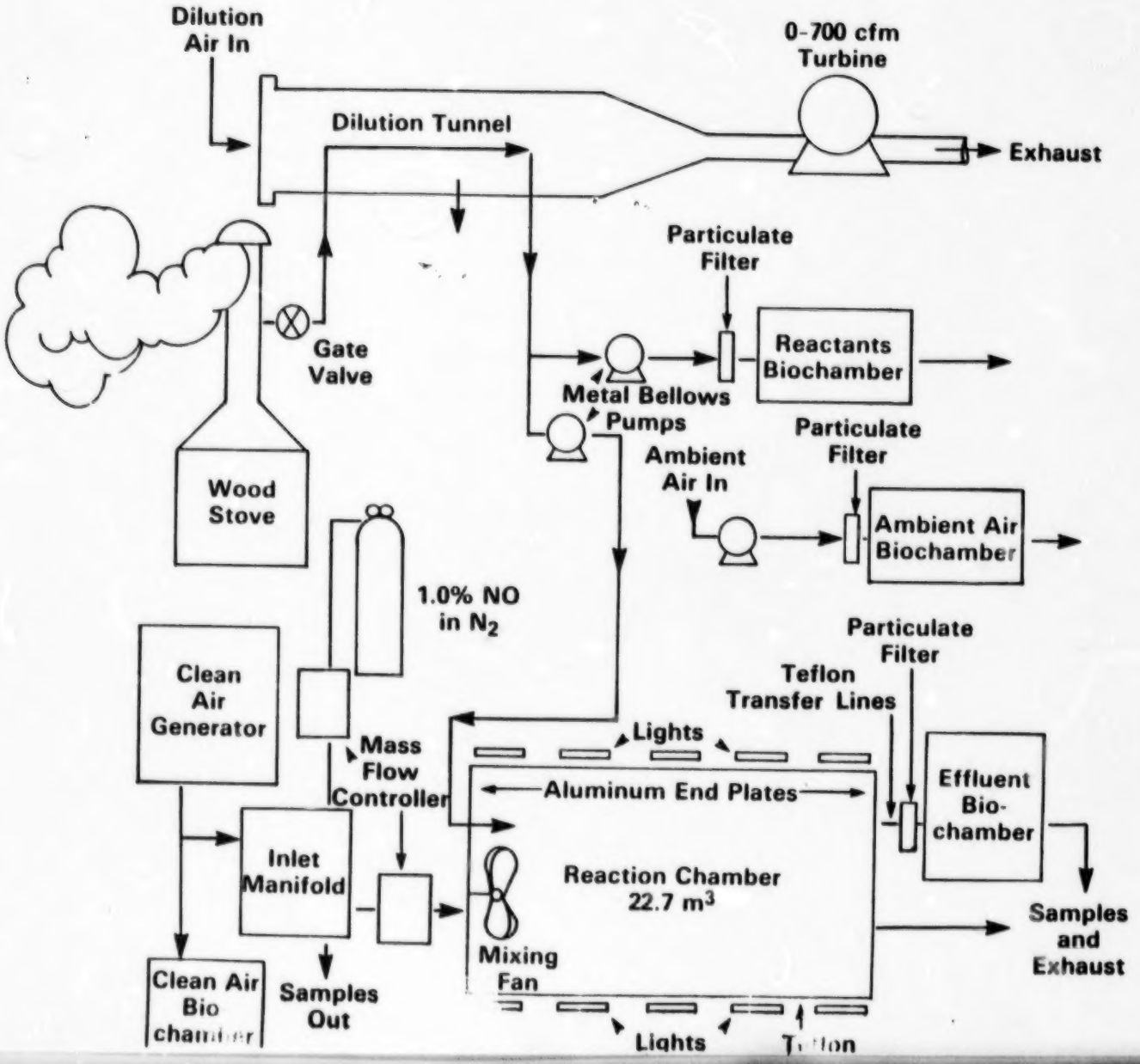
Species	Experiment A (No NOx Added)		Experiment B (NOx Added)		Experiment C (NOx Added)	
	Initial	Final	Initial	Final	Initial	Final
Nitric Oxide	75	0	454	0	461	0
NO_x	135	64	657	252	576	259
Ozone	0	79	0	467	0	696
CO (ppm)	33.5	32.0	38.0	33.4	38.7	35.5
Ethylene	702	652	537	313	847	439
Benzene	68	62	62	50	102	68
Toluene	27	16	62	15	24	10
Formaldehyde	325	381	269	365	229	383
Acetaldehyde	140	106	88	109	57	75
PAN	0	52	0	174	0	232
HC (ppm-C)	20.6	19.1	16.4	13.2	17.2	15.0
HC/NO_x	153		25		30	

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus used in the IACP wood smoke study.

Figure 2. Graphical comparison of the mutagenicity of the gas- and particulate-phase components of wood smoke, before and after irradiation. (The mutagenicity was measured without metabolic activation and is expressed in units of revertants per cubic meter.)

Experimental Schematic of the Wood Stove, Reaction Chamber, and Exposure Apparatus



Gas and Particulate Phase Mutagenicity of Dilute Wood Smoke + NOx in Air